Kinetic modeling studies of CO oxidation in the presence of H_2 over $Pt/Rh/Al_2O_3$ catalysts

2011 DOE Crosscut Workshop on Lean Emissions Reduction Simulation

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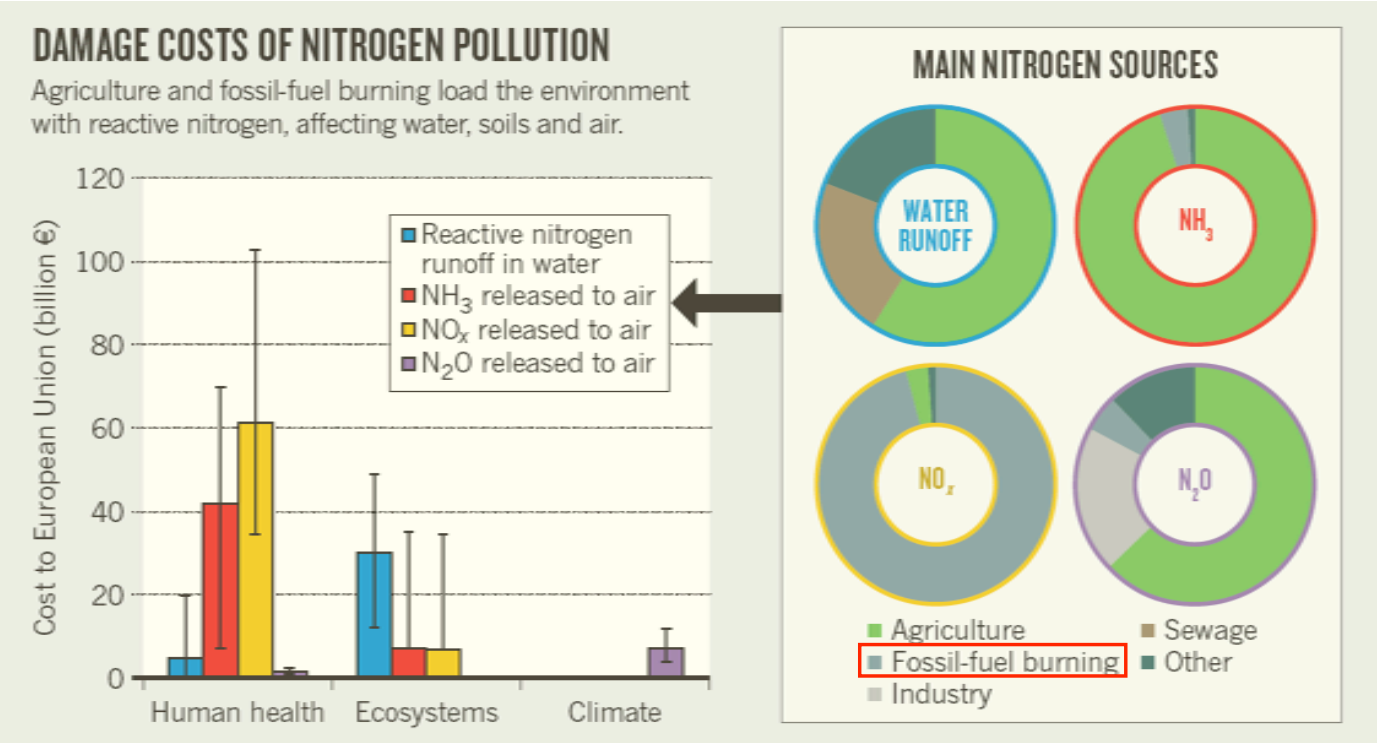
Outline

- Research drivers and objectives
- Kinetic Modeling in the *IFP Exhaust* library
- Modeling strategy
  - Assessing CO oxidation on $Pt/Rh/Al_2O_3$ in the presence of H_2
  - Globalization: from microkinetics to global kinetic rates
- Conclusions & perspectives

Research drivers

***Curbing nitrogen emissions is a central environmental challenge for the twenty-first century* [Sutton *et al.*]**



Sutton *et al.* *Nature*, April 2011, Copyright © 2011, Nature Publishing Group

Objectives

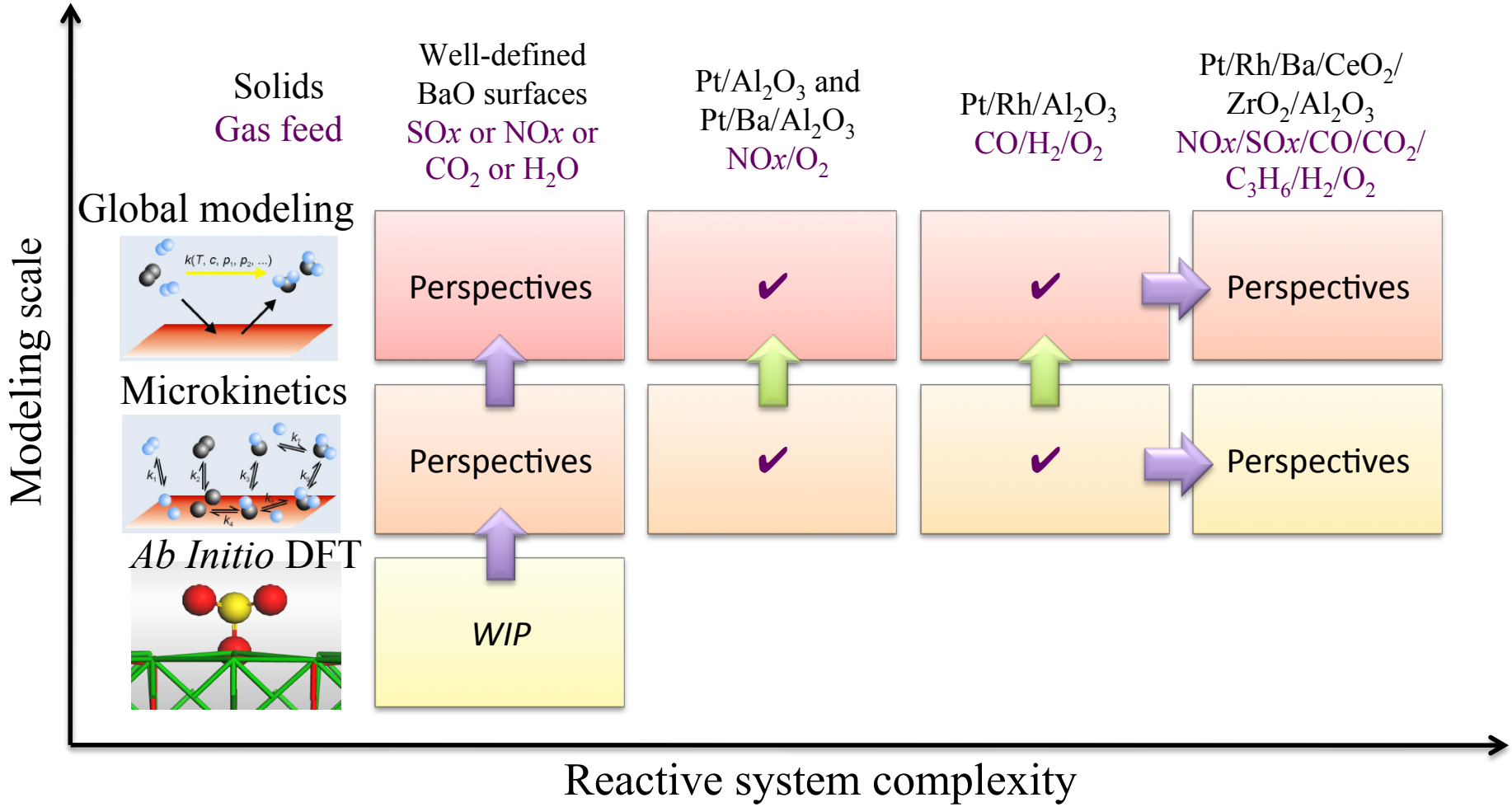
- **Long-term goal: understanding and modeling the fundamental chemistry involved in the LNT operating cycle**
  - NO oxidation over Pt/Al_2O_3
  - NO*x* storage over Ba/Al_2O_3
  - Pt-Ba interactions: spillover

  → **CLEERS 2010**
  - **CO and H_2 oxidation over Pt/Al_2O_3**
  - **More complex catalyst formulations: $Pt\text{-}Rh/Al_2O_3$ and $Pt\text{-}Rh/CeO_2/Al_2O_3$**
  - Hydrocarbon oxidation chemistry
  - Nitrate regeneration and NO*x* release
  - Sulfur poisoning

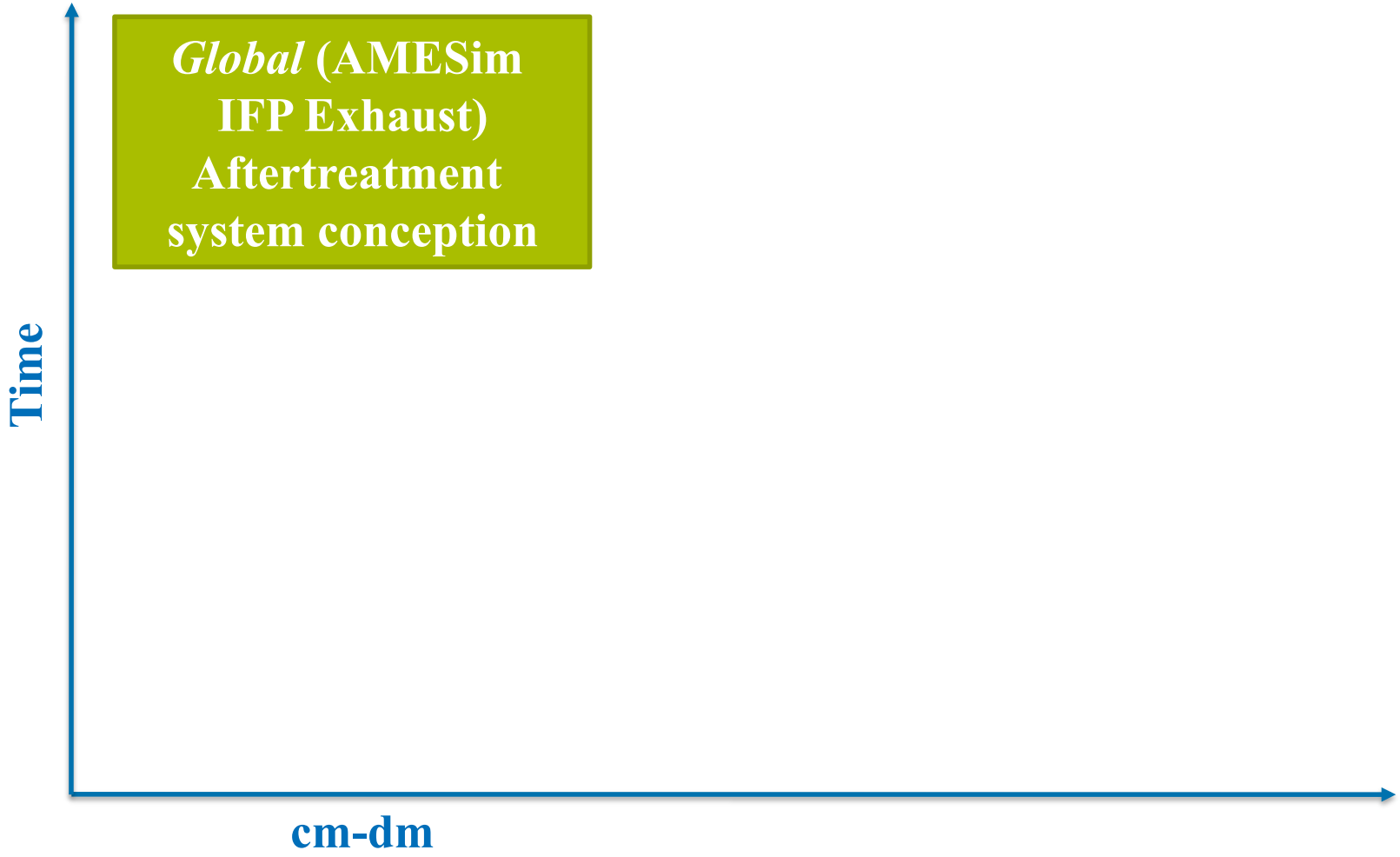
  → **Outlook 2012**

After-treatment modeling @ IFPEN

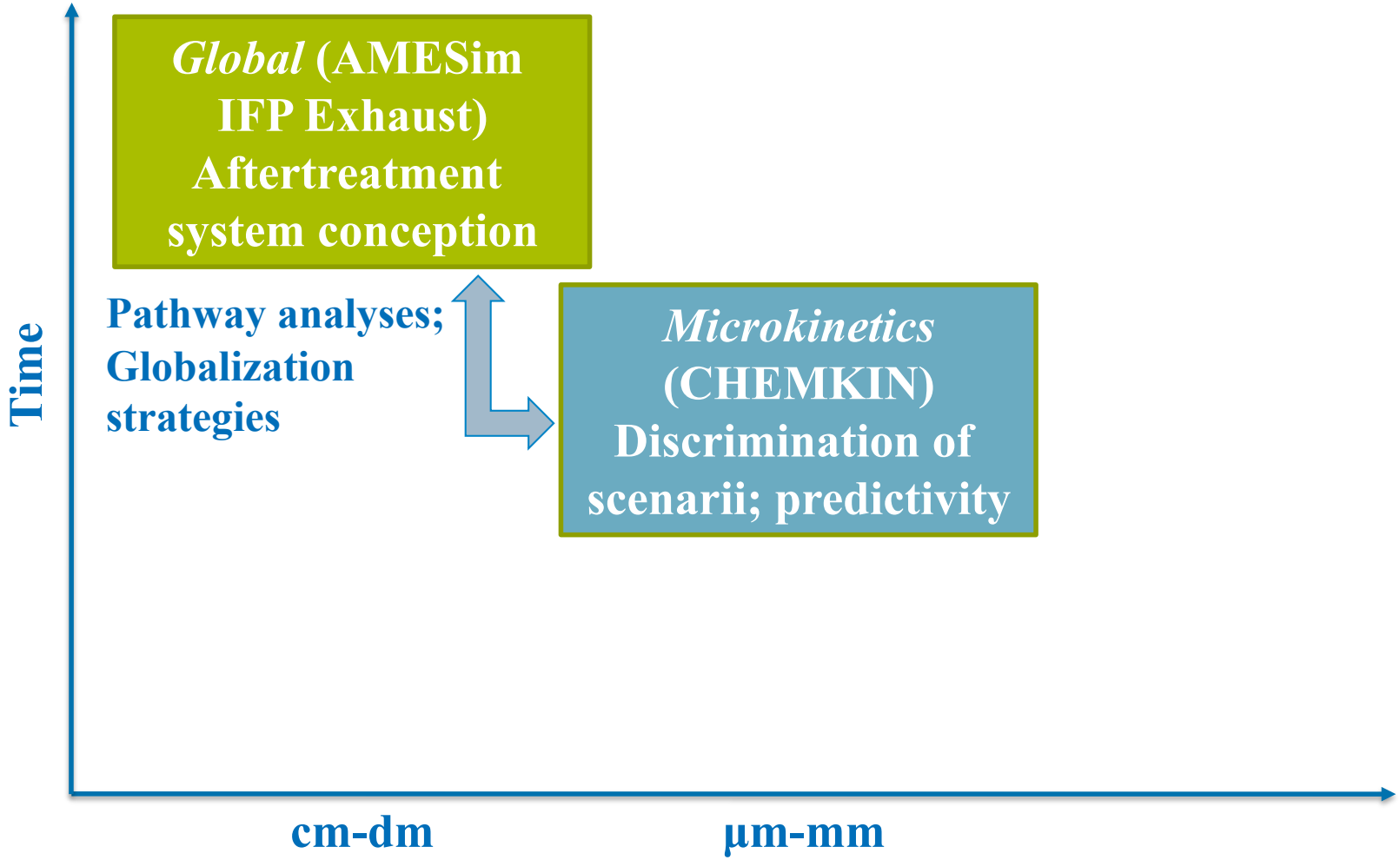
Multiscale approach



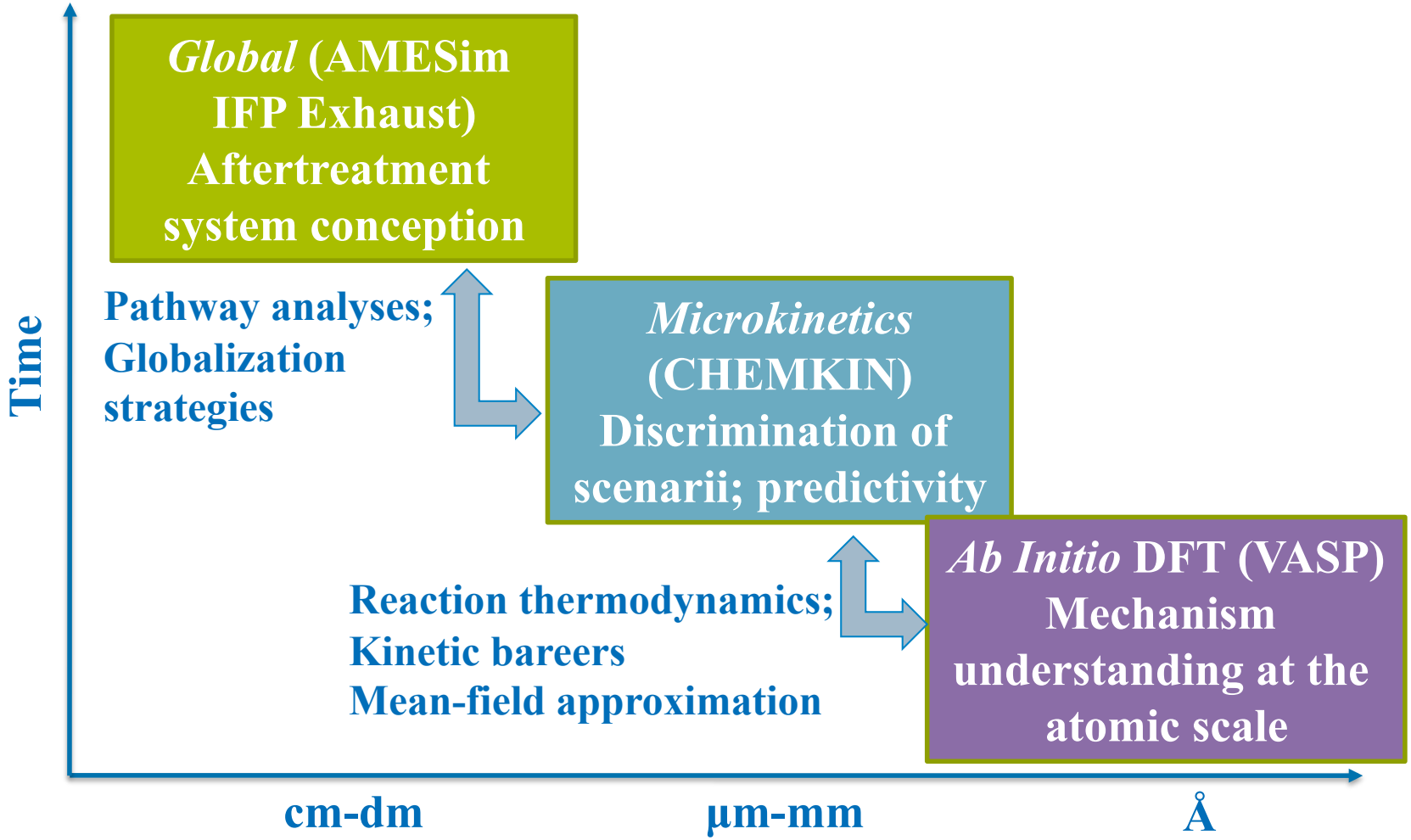
Multiscale methodology



Multiscale methodology



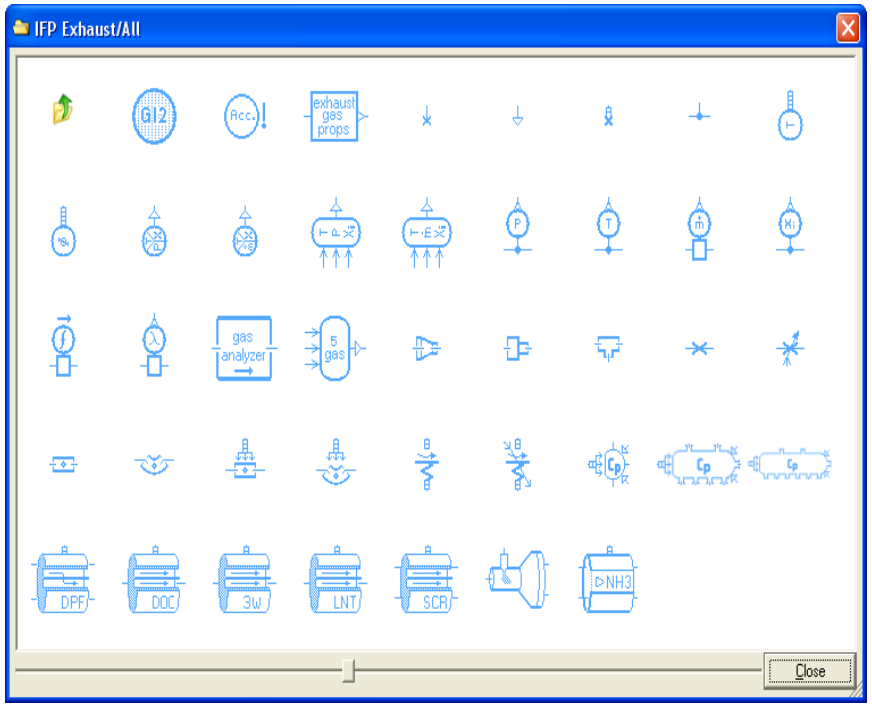
Multiscale methodology



The IFP-Exhaust library

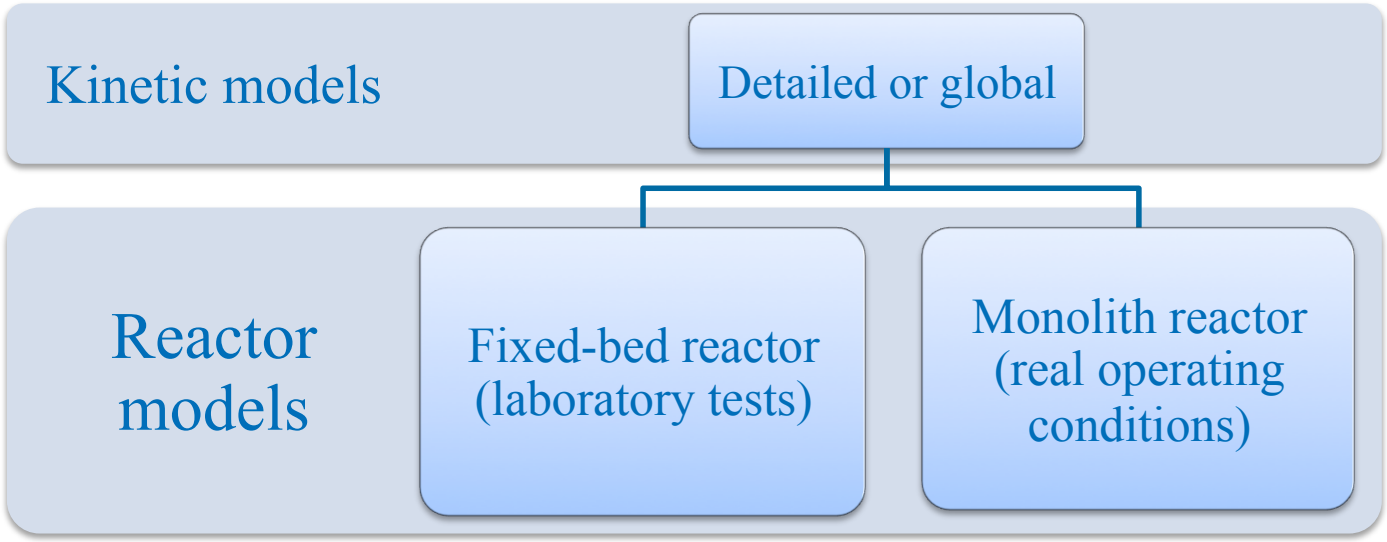
Library for after-treatment system modeling

- **Main components :**
  - Sensors / sources
  - Throttle, pipes
  - Volumes, manifolds
  - Heat transfers models
  - 3-way catalyst (3WC)
  - Diesel Oxidation Catalyst (DOC)
  - Diesel Particulate Filter (DPF)
  - Lean NO*x*-Trap (LNT)
  - Selective Catalytic Reduction (SCR) system



AMESim modeling platform

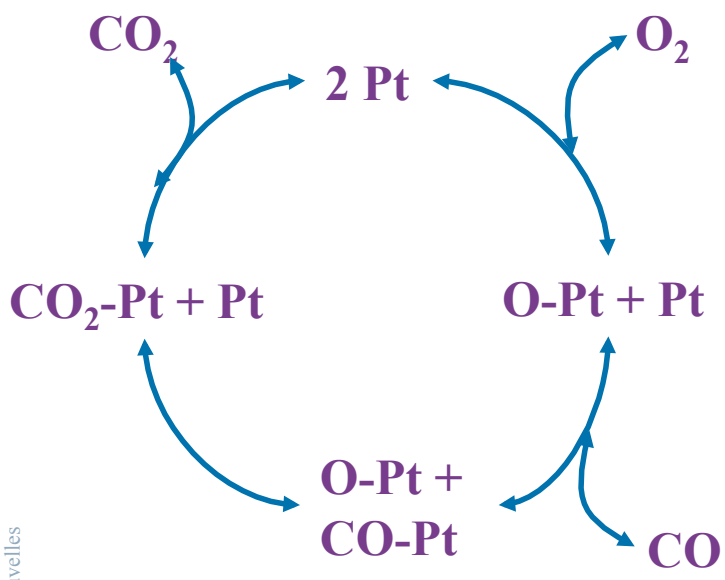
- **Kinetic model validation for various experimental configurations:**



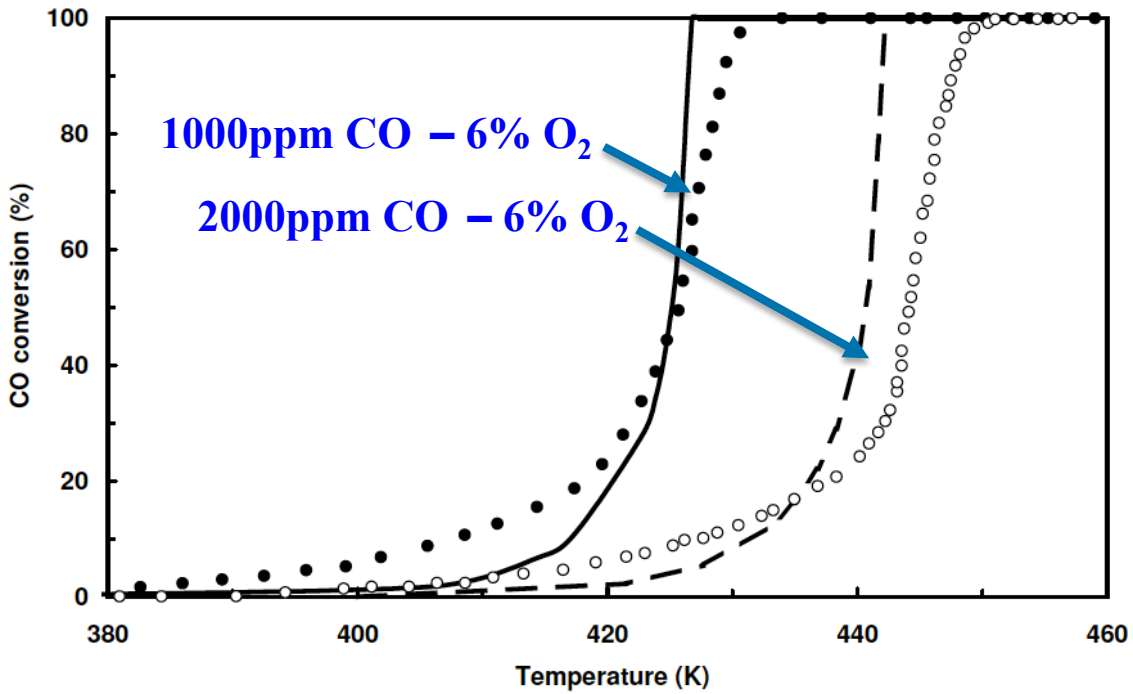
- **Macro-mixing properties**
  - ***N* 0D reactors in series: axial dispersion accounted for (pseudo-1D approach)**

CO oxidation on Pt/Al_2O_3: microkinetic scheme

- **Elementary reactions compiled from the literature data and adjusted to fit different experiments**



Model performances against experimental points (Salomons *et al.*)



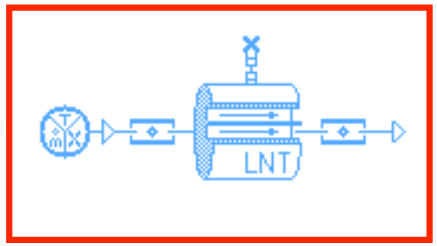
CO oxidation on Pt/Al_2O_3: global scheme

- **Globalization strategy:**
  - **Rate analyses showed the rate-determining step over a wide temperature range is the surface CO-Pt oxidation**

$$\text{CO-Pt} + \text{O-Pt} \xrightarrow{A} \text{CO}_2\text{-Pt} + \text{Pt}$$

  - **Developing a Langmuir-Hinshelwood-type oxidation rate based on microkinetic parameters:**

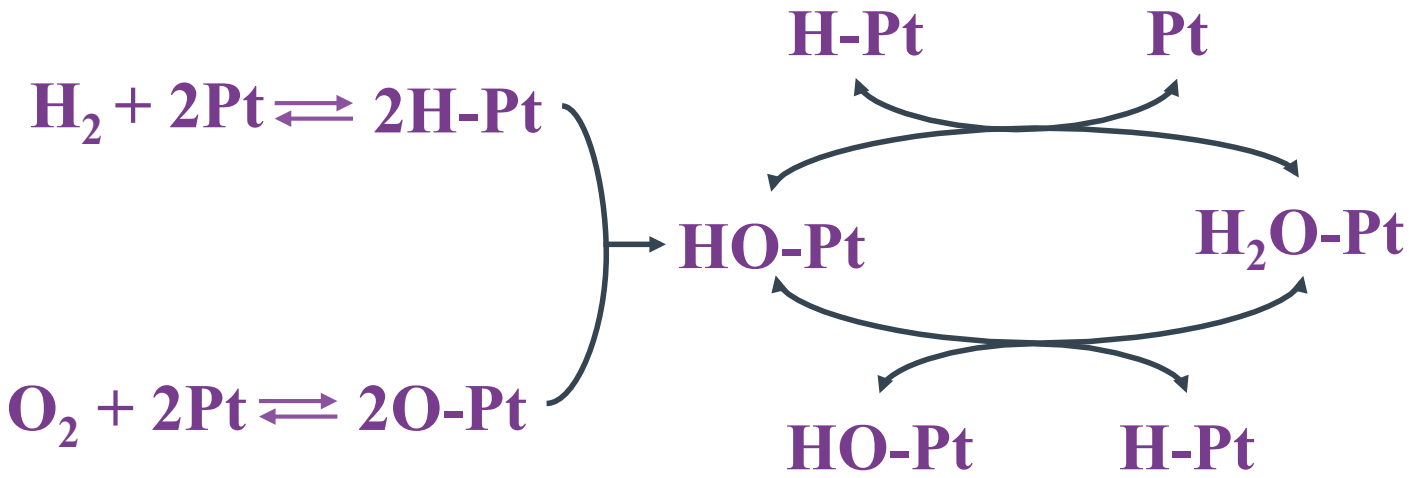
$$r_{CO,oxid} = \frac{k_{glob}\left(K_{CO}x_{CO}\right)^{\alpha}\left(K_{O_2}x_{O_2}\right)^{\beta}}{\left[1+\left(K_{CO}x_{CO}\right)^{\alpha}+\left(K_{O_2}x_{O_2}\right)^{\beta}\right]^{\gamma}}$$

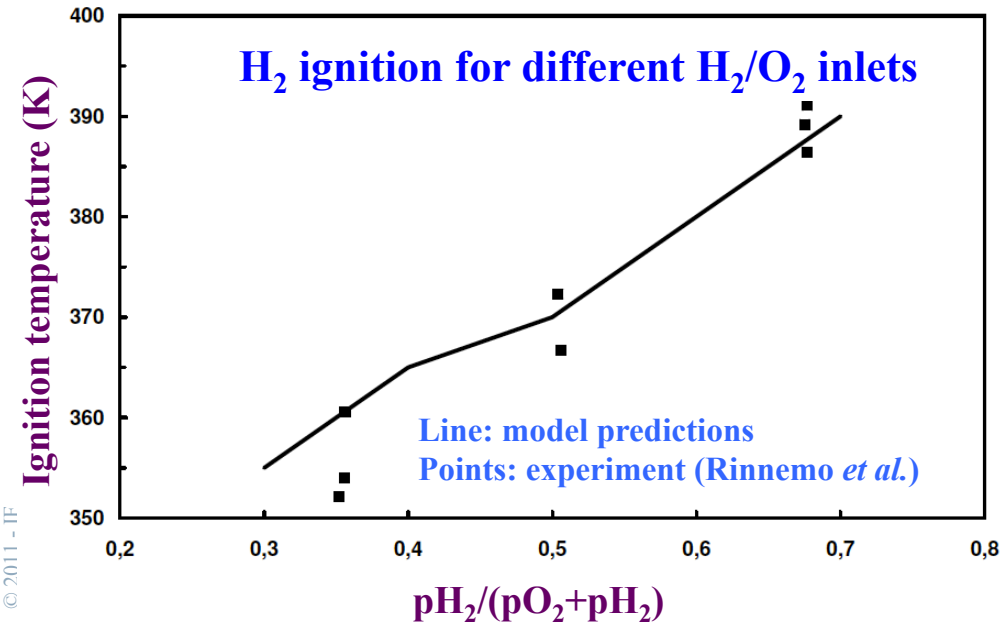


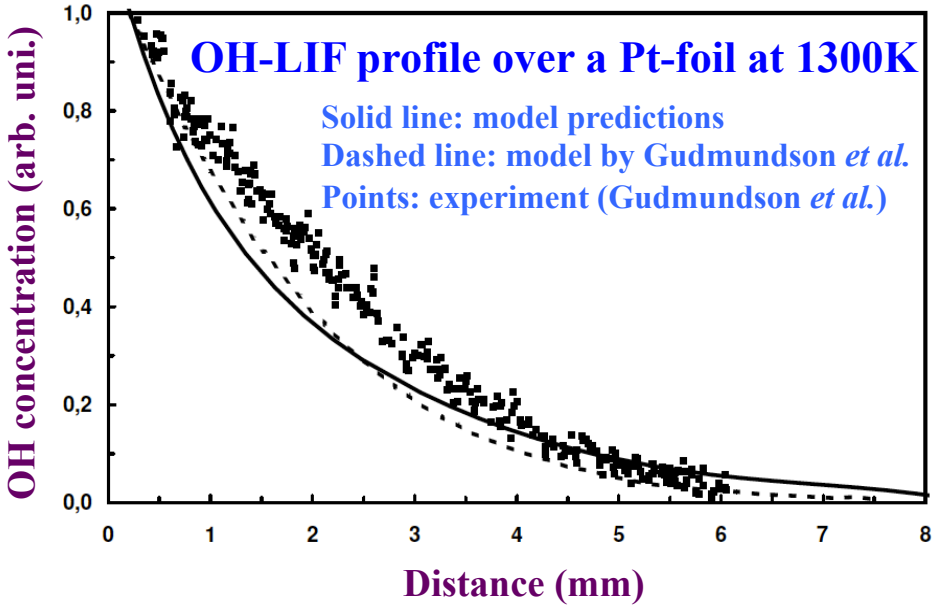
To IFP Exhaust library

k_{glob} – global rate constant
K_{CO} – equilibrium constant for CO adsorption
K_{O2} – equilibrium constant for O_2 adsorption

H_2 oxidation on Pt/Al_2O_3: microkinetic scheme

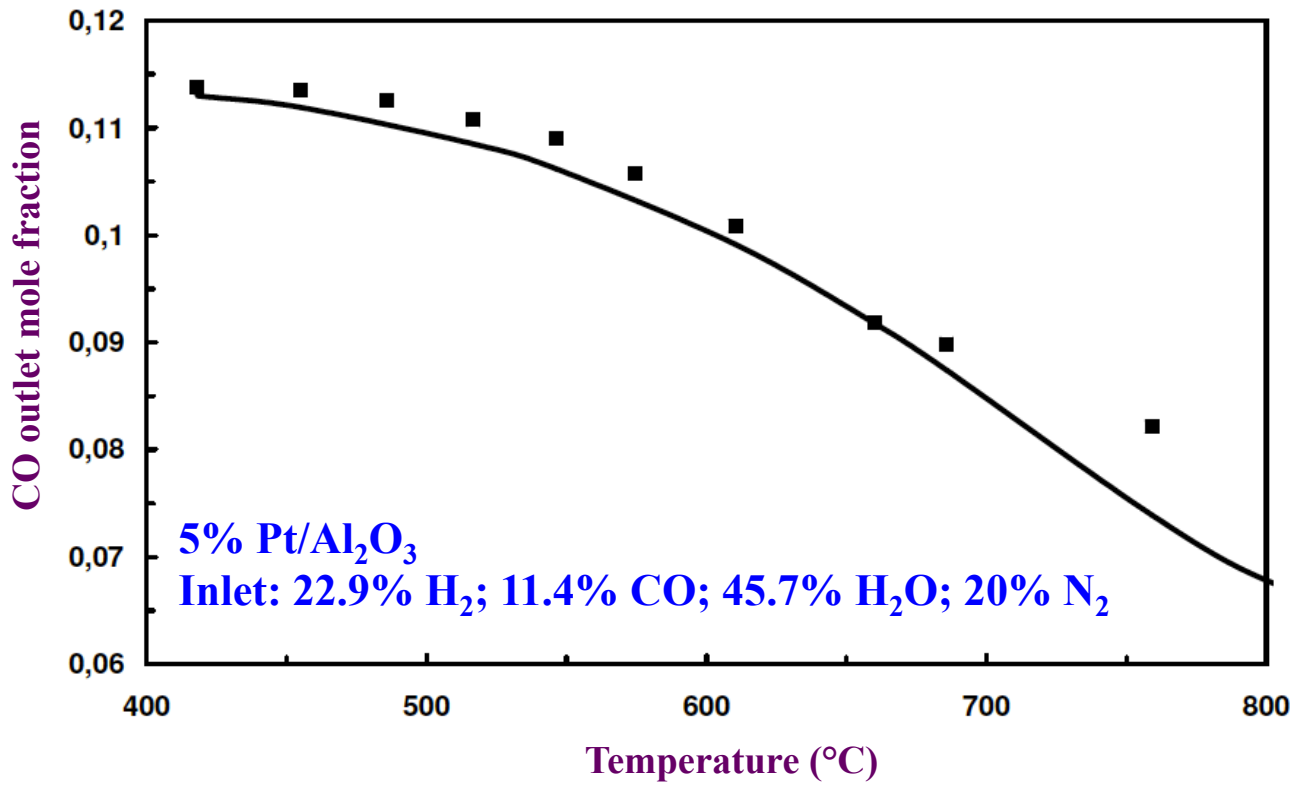






CO-H_2 interplay on Pt/Al_2O_3

- **Microkinetic scheme (18 elementary steps):**
  - **CO-Pt oxidation by HO-Pt to CO_2-Pt**
  - **COOH-Pt and HC-$(OPt)_2$ formation**
- **Validation against water-gas shift data (Wheeler *et al.*)**



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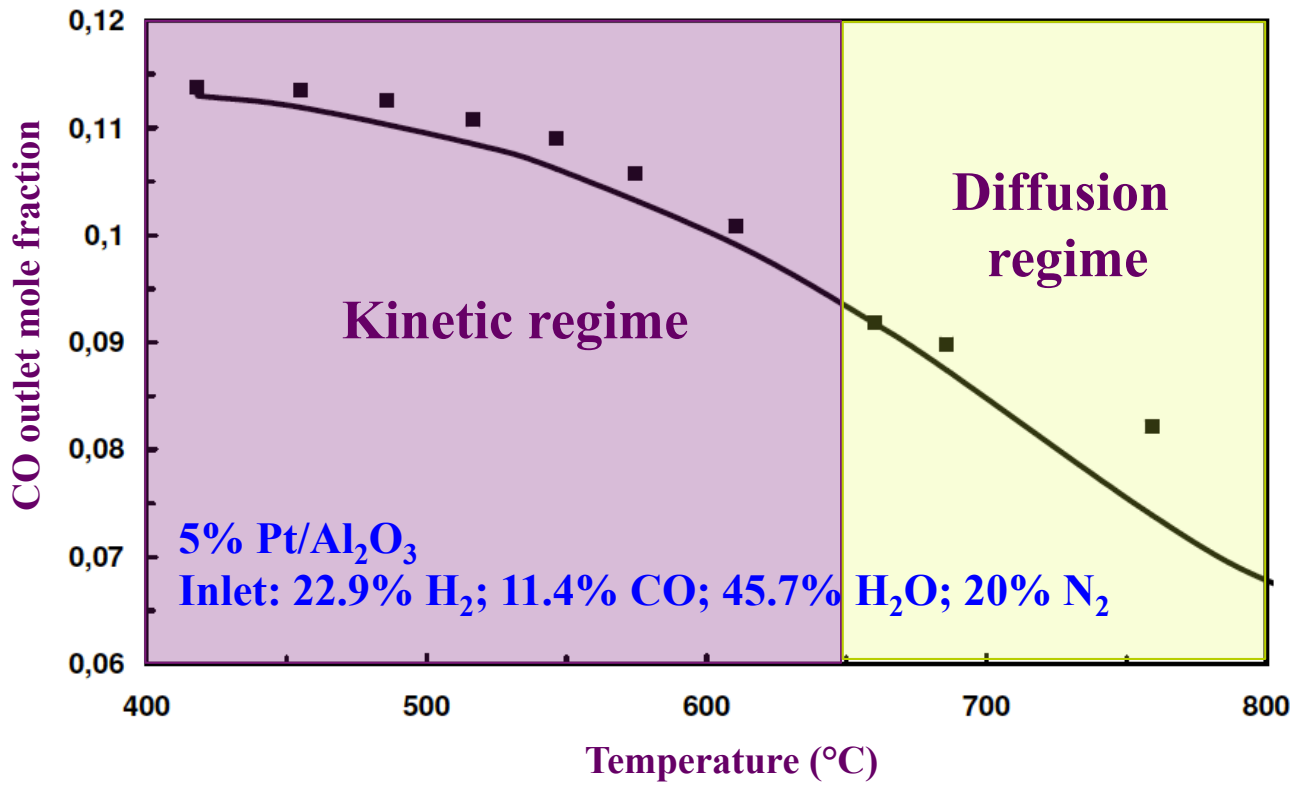


Impact of H_2 on CO light-off temperatures

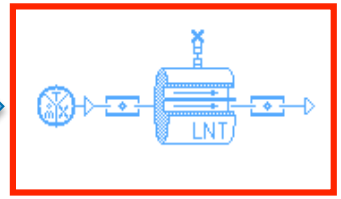
- **Microkinetic scheme:**
  - **Hydrogen-dependent CO desorption:**

$$\mathbf{CO + Pt \rightleftharpoons CO\text{-}Pt} \qquad E_{act} = E^{0}_{act}(1 - \alpha\,\Theta_{H-Pt})$$

- **Global scheme:**
  - **CO consumption by an intermediary HO-Pt species:**

$$\mathbf{CO\text{-}Pt + HO\text{-}Pt \rightleftharpoons CO_2\text{-}Pt + H\text{-}Pt}$$

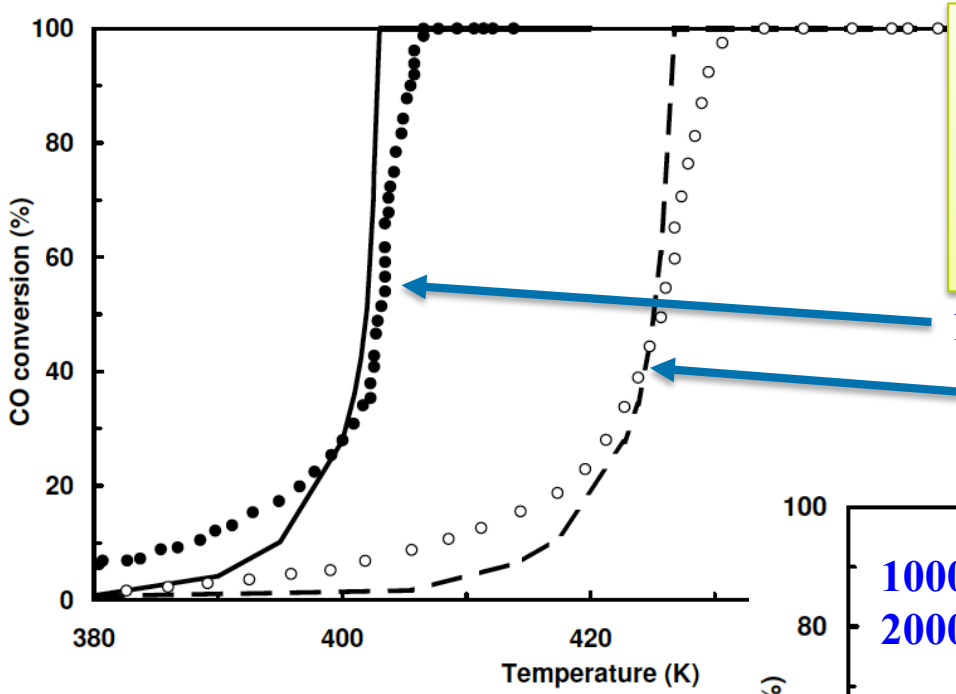
$$r_{CO,oxid} = \frac{k_{glob}\left(K_{CO}x_{CO}\right)^{\alpha}\left(K_{O_2}x_{O_2}\right)^{\beta} + k_{H_2}\left(K_{H_2}x_{H_2}\right)^{\delta}}{\left[1+\left(K_{CO}x_{CO}\right)^{\alpha}+\left(K_{O_2}x_{O_2}\right)^{\beta}\right]^{\gamma}}$$



To IFP Exhaust library

***k_{H2} and K_{H2}* obtained directly from microkinetic data**

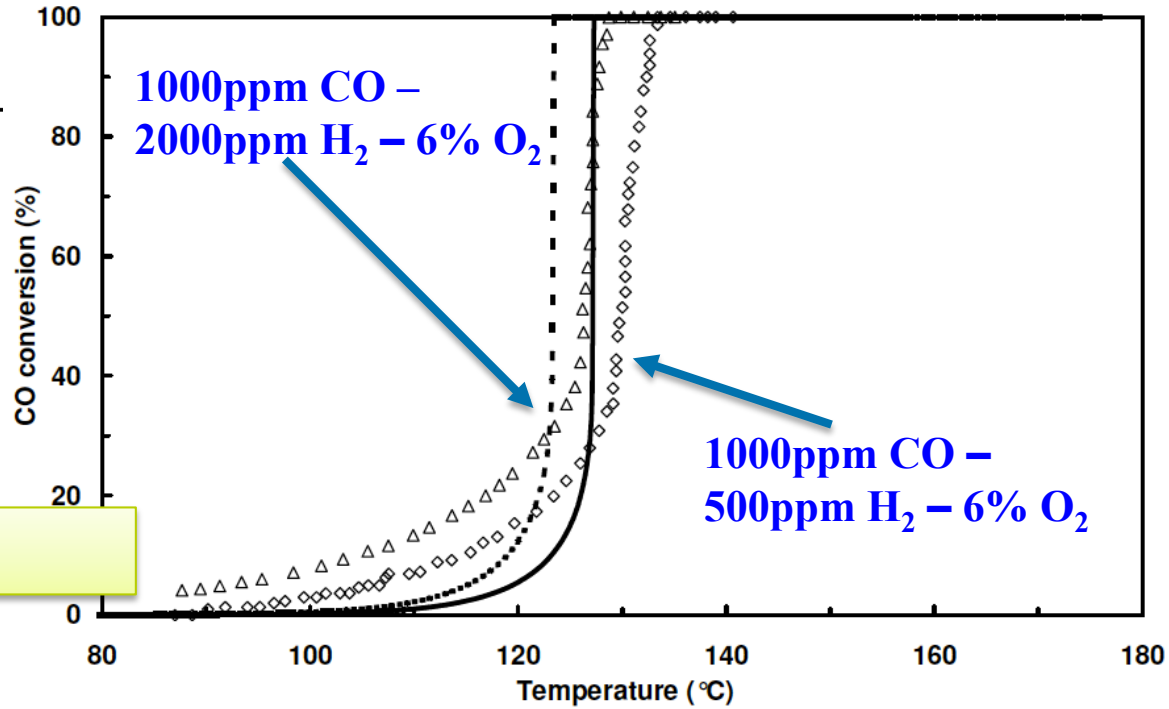
Impact of H_2 on CO light-off temperatures



Microkinetic model
Lines: calculated CO conversion
Points: experimental CO conversion
(Salomons *et al.*)

1000ppm CO – 500ppm H_2 – 6% O_2

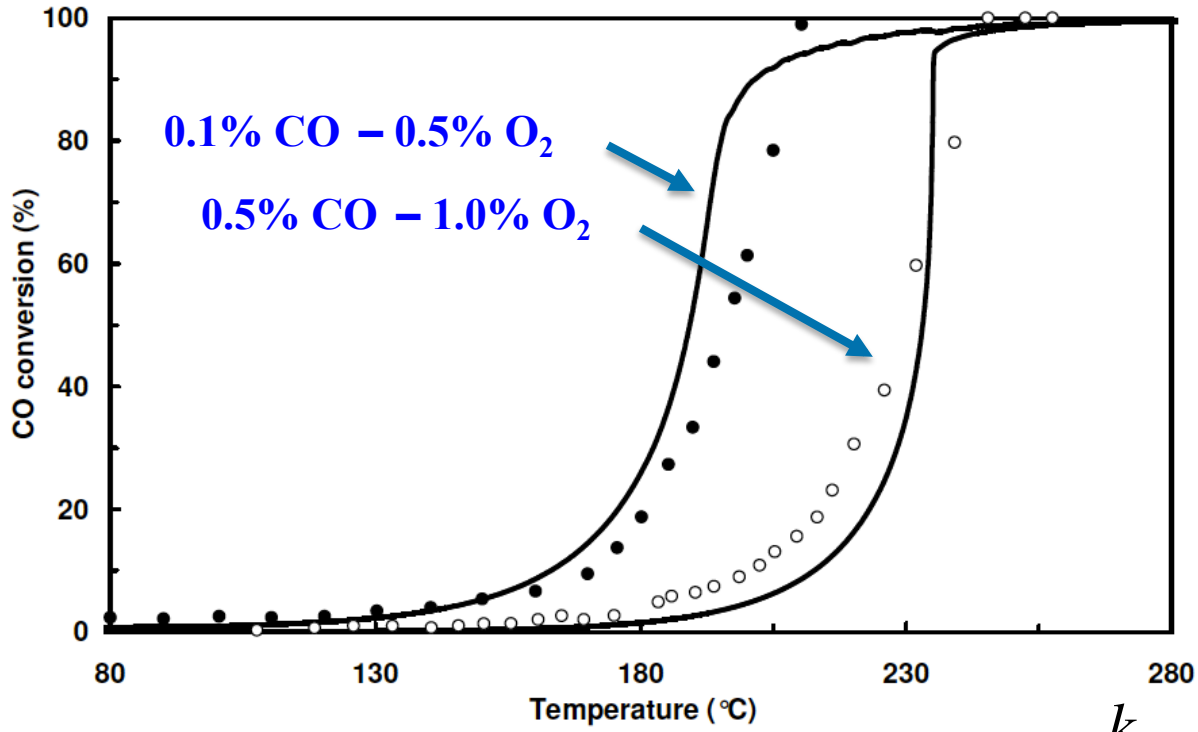
1000ppm CO – 6% O_2



Global model

CO oxidation on Rh/Al_2O_3

- **Microkinetic model (10 elementary steps) used for the conception of a global Langmuir-Hinshelwood rate law**

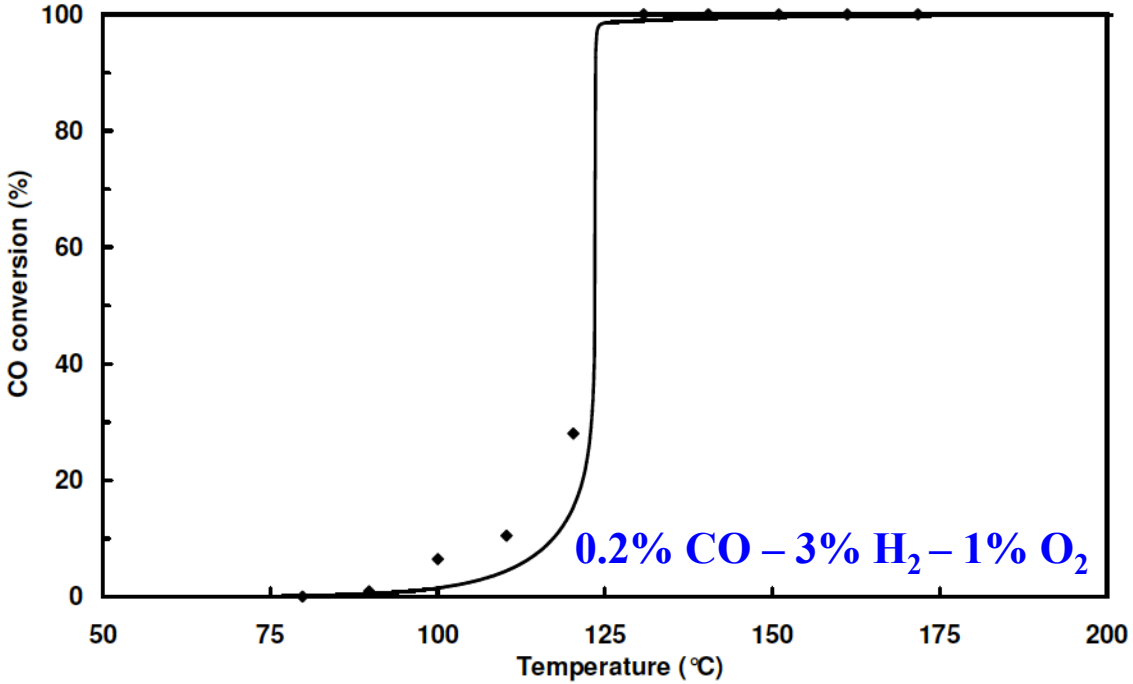


Model performances against experimental points (Cai *et al.*)

$$r_{CO,oxid} = \frac{k_{glob}\left(K_{CO}x_{CO}\right)^{\alpha}\left(K_{O_2}x_{O_2}\right)^{\beta}}{\left[1+\left(K_{CO}x_{CO}\right)^{\alpha}+\left(K_{O_2}x_{O_2}\right)^{\beta}\right]^{\gamma}}$$

CO-H_2 interplay on Rh/Al_2O_3

- **Microkinetic model (18 elementary steps) used for the conception of a global Langmuir-Hinshelwood rate law**



$$r_{CO,oxid} = \frac{k_{glob}\left(K_{CO}x_{CO}\right)^{\alpha}\left(K_{O_2}x_{O_2}\right)^{\beta} + k_{H_2}\left(K_{H_2}x_{H_2}\right)^{\delta}}{\left[1+\left(K_{CO}x_{CO}\right)^{\alpha}+\left(K_{O_2}x_{O_2}\right)^{\beta}\right]^{\gamma}}$$

Model performances against experimental points (Ito *et al.*)

Conclusions & perspectives

- **Detailed kinetic models for CO oxidation in the presence of H_2 were conceived for Pt/Al_2O_3 and Rh/Al_2O_3 model catalysts**
- **Globalization strategies allowed transposing microkinetic data directly into global models**
- **Assembling Pt and Rh blocks for simulating bimetallic catalytic formulations**
- **Toward more complex supports: effect of CeO_2 and ZrO_2**

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